Transferability–Additivity of Molar Volumes of Organic Liquids and Their Relation to Normal Boiling Points

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The molar volumes at 20 °C of the sequences *n*-RH, cycloalkanes, *n*-RF, *n*-RCl, *n*-RBr, *n*-RI, *n*-RCN, *n*-ROH, *n*-RSH, *n*-RNH_2, *n*-RCOOH, *n*-RCOOMe, *n*-RCOOEt, *n*-ROAc, *n*-R^1SR^2-*n*, *n*-RCOMe, $Cl(CH_2)_nCl$, $Br(CH_2)_nBr$, and *n*-$RCH{=}CH_2$ have been correlated with the corresponding carbon numbers in the *n*-alkyl group or in $X(CH_2)_nX$. These correlations imply that the molar volumes (MV) of sequences of monosubstituted hydrocarbon derivatives are interrelated. The space requirement of a methylene group in a compound *n*-RY exhibits a small but significant dependence on the substituent Y as well as on secondary structural changes on Y, e.g., Y = COOMe vs COOEt. A phenomenon analogous to reaction thermoneutrality has been observed; in disproportionation or redistribution organic reactions, in which the number of molecules remains constant and the involved molecules do not exhibit strong hydrogen bonds, the sum of the MV's of the reactants is nearly equal to the sum of MV's of the products. This phenomenon which is termed "choroneutrality" allows the estimation of MV's and/or densities. Molar volumes of di- and trichloromethanes are linearly related to the respective normal boiling points. The ratios V_M/T_b behave like the corresponding thermochemical parameters, $\Delta H_v/T_b$ or $\Delta H_f/T_b$. Namely, they plot linearly against the corresponding carbon numbers. Molar volumes of normal hydrocarbons are shown to correlate well with the recently reported solubilities of C_{60} in the same solvents.

Introduction

There is a common feeling among organic chemists that in a compound such as, e.g., $CH_3CH_2CH_2CH_2COOMe$ (I), the methylene group α to the carboxy group is entirely different from the other methylene groups in the molecule and even more so from the ω-methyl group. This feeling is based on the experience that, for example, the C_2 exhibits the highest carbon acidity, undergoes regiospecific halogenation, and may be distinguished by its NMR parameters. There are, however, a number of molecular parameters of compounds such as I, for which all methylene groups are "equivalent", including the methylene in the ω-methyl group. These parameters exhibit linear dependence on the carbon number of the members with normal alkyls within a given homologous series. To this category belong enthalpies of formation,[1] enthalpies of vaporization,[2,3] zero point energies,[4] Trouton's ratios,[3] enthalpies of sublimation,[5] and molecular refractivities (or polarizabilities).[6] These linear relationships usually hold even for the first member of the series, i.e., for carbon number $n = 1$, and therefore, they suggest that a homologous series of, e.g., compounds like I, could be viewed as $H(CH_2)_nCOOMe$. Thus, all methylene groups appear to be equivalent as far as their contribution to the molar value of the parameter under consideration is concerned. The magnitude of the methylene contribution is expressed by the slope of the (Parameter) vs *n* straight line, whereas, the intercept of the straight line should be related to the contribution of the "parent" compound, e.g., HCOOMe in the above given example.[3] Thus, in all the above-mentioned cases the contribution of a methylene group to the molar value of a molecular parameter is said to be transferable and additive in an intraseries fashion. To the above list of molecular parameters should now be added the parameter "molar volume". Molar volume, namely the quotient of the molecular weight and the density ($V_M = M/\rho$), is related to molecular refractivity and polarizability through the Lorentz–Lorentz equation (1),[7] as well

$$(n^2 - 1)/(n^2 + 2)V_M = 4/3\,\pi N \alpha \qquad (1)$$

$$\delta^2 = (\Delta H_v - RT)/V_M \qquad (2)$$

as to the cohesive energy density function[8] (2), the square root of which is known as the solubility parameter.[8] The cohesive energy function is used in multiparameter expressions for correlating solvent effects on rates and equilibria,[9] whereas the solubility parameter function is used for rationalizing solubility properties.[10] Theoretical calculations have shown that the volume of a methylene group in normal hydrocarbons is a transferable and additive parameter.[11] Molar volume may be the first molecular parameter in the history of chemistry to be shown to exhibit the property of additivity and transferability. Kopp,[12] between 1839 and 1855, determined the

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[1] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970; p 518.

[2] Mannson, M.; Sellers, P.; Stridh, G.; Sunner, S. *J. Chem. Thermodyn.* **1977**, *9*, 91.

[3] Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1991**, *56*, 1615.

[4] Pitzer, K. S.; Catalano, E. *J. Am. Chem. Soc.* **1956**, *78*, 4844.

[5] Davies, M. *Some Electrical and Optical Aspects of Molecular Behaviour*; Pergamon Press: Oxford, 1965; p 171.

[6] See, e.g.: Brand, J. C. D.; Speakman, J. C. *Molecular Structure, the Physical Approach*; Edward Arnold Publisher LTD: London, 1964; p 94.

[7] See, e.g.: Kauzmann, W. *Quantum Chemistry*; Academic Press: New York, 1957; p 603.

[8] (a) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand-Reinhold: Princeton, 1970. (b) Dack, M. R. J. *Chem. Soc. Rev.* **1975**, *4*, 211. The latter reference includes additional physicochemical parameters involving molar volumes.

[9] Abraham, M. H.; Grellier, P. L.; Abboud, J.-L. M.; Doherty, R. M.; Taft, R. W. *Can. J. Chem.* **1988**, *66*, 2673. Gajewski, J. J. *J. Org. Chem.* **1992**, *57*, 5500.

[10] See, e.g.: Sivaranam, N.; Dhamodaran, R.; Kaliappan, I.; Srinivasan, T. G.; Vasudeva Rao, P. R.; Mathews, C. K. *J. Org. Chem.* **1992**, *57*, 6077.

[11] Bader, R. F. W.; Carroll, M. T.; Cheesman, J. R.; Chang, C. *J. Am. Chem. Soc.* **1987**, *109*, 7968.

[12] Kopp, H. *Ann. Phys.* **1839**, *47*, 133; *Ann.* **1855**, *96*, 153.

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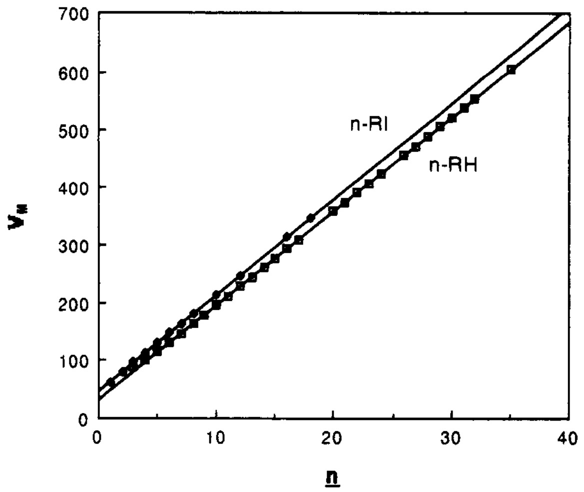

Figure 1. Molar volumes of normal hydrocarbons and of *n*-alkyl iodides plotted against the corresponding carbon numbers.

molar volumes of a number of organic compounds at their normal boiling point, and he was able to predict molar volumes to a very satisfactory degree of approximation by assigning atomic and functional group contributions to the molar volume. This and subsequent work by other investigators has been reviewed.[13] From this review, of particular significance to the present work are (a) the observed linearity between molar volumes at 20 °C and carbon numbers for the homologous series of paraffins and esters and (b) the linearity between densities and boiling points of a sequence of organic compounds.

We wish to report some other remarkable regularities of molar volumes in general and, in particular, the contribution of a methylene group to the molar volume for various classes of organic compounds. We also discuss some properties and trends of molar volumes and demonstrate their relevance to normal boiling points. It should be pointed out that this work is related to matters that are examined in a review concerning "the size of molecules".[14]

Interrelation of Molar Volumes. We have considered the molar volumes[15] at 20 °C of homologous sequences of organic liquids. For example, for the series of *n*-alkyl iodides from C_2 to C_8 the molar volumes are 80.57, 97.20, 113.92, 130.63, 147.25, 163.95, and 180.59 cm^3. It can be seen that there is a monotonous increase from one member of the series to the next by ca. 16.6 cm^3 per methylene group. This behavior is reminiscent of the thermochemical parameters[1–5] which for the members of a homologous series with n-alkyl groups plot linearly against the corresponding carbon numbers *n*. Exactly the same holds for the molar volumes of any homologous series of organic compounds, e.g., Figure 1. Analogous correlations are given in the form of regression equations in Table I.

Table I. Regression Equations of Plots (Molar Volumes at 20 °C) versus (Carbon Number) of *n*-Alkyl Derivatives and of $X(CH_2)_nX$

entry	series	slope	intercept	*r*	range of *n*
1	*n*-RH	16.318	32.308	1.000	4–17, 20–35
2	cycloalkanes	13.353	27.610	1.000	5–8, 10
3	*n*-RF	16.052	34.974 (20.27)[a]	0.999	1–8, 10, 16
4	*n*-RCl	16.420	38.827	1.000	1–10, 12, 14, 16, 18
5	*n*-RBr	16.555	41.155	1.000	1–8, 10, 12–14, 16–18
6	*n*-RI	16.632	47.162	1.000	1–8, 10, 12, 16, 18
7	*n*-RCN	16.596	37.200 (38.67)	1.000	1–8, 11–13, 15–17
8	*n*-ROH	16.629	24.833 (18.02)	1.000	1–11
9	*n*-RSH	16.554	40.696	1.000	1–8, 10, 18
10	*n*-RNH_2	16.577	32.266	1.000	1–16
11	*n*-RCOOH	16.760	41.176 (37.73)	1.000	1–8
12	*n*-RCOOMe	16.691	63.210 (61.64)	1.000	1–7, 9, 11
13	*n*-RCOOEt	16.681	81.408 (80.80)	1.000	1–11
14	MeCOOR-*n*	16.745	64.141 (57.23)	1.000	1–5, 8, 10
15	*n*-R^1SR^2-*n*	16.707	40.499	1.000	2–6, 8, 10, 14
16	*n*-RCOMe	16.727	56.419 (56.23)	1.000	1–10
17	$Cl(CH_2)_nCl$	16.182	47.363	1.000	1–6
18	$Br(CH_2)_nBr$	16.549	53.056 (51.237)	0.999	1–5
19	*n*-$RCH{=}CH_2$	15.952	62.652	1.000	1–3, 6, 8, 10, 14

[a] In parentheses is given the corresponding molar volume of the "parent" compound at 20 °C. For example, the parent compound of *n*-RCOOMe is HCOOMe and of CH_3COOR-*n* is CH_3COOH.

It can be seen from the data in Table I that the molar volumes of *n*-alkyl derivatives of all classes of compounds correlate perfectly with the respective carbon numbers. It should be noted, however, that the same correlations can accommodate the molar volumes of the branched alkyl isomers but with poorer correlation coefficients. This is because the molar volumes (MV) of isomeric compounds differ relatively little, ca. 5% for the C_4 isomers and even less for the higher ones. The reported[13] relationship $V_M = 16.72n + 32.05$ for the paraffins is considerably different from ours, entry 1, Table I. It seems that all isomeric hydrocarbons were been included in the former correlation. By including only the *n*-alkyl derivatives in the correlation, and since the point for C_1 derivative is on the regression line we can consider a *n*-RX compound as $H(CH_2)_nX$ and assign a meaning to the slope and the intercept of the regression equations. The slope represents the methylene group contribution to the molar volume (MV), whereas the intercept corresponds to the MV of the "parent" compound HX. Thus, *n*-RX compounds are no different from the symmetrical ones, $X(CH_2)_nX$. It should be mentioned here that the MV's of, e.g., the secondary isomers within a homologous series should, and do, plot linearly against the corresponding carbon numbers. Indeed, these isomers, according to the above analysis, could be represented as *n*-RCH(X)Me or $H(CH_2)_nCH(X)Me$. It is evident from Table I that, except for entry 2, the methylene group contribution to the MV is a little more than 16 cm^3. It is felt that the very good correlation coefficients indicate that the observed differences among the slopes in Table I, although small, are significant and reflect the dependence of the volume of a methylene group with respect to the functional group attached to the *n*-alkyl group. This can be seen better in the case of alkyl halides, entries 3–6, Table I. We notice that the slope increases with decreasing electronegativity or increasing polarizability of the halogen in *n*-RX. In fact, by plotting the slopes of the regression lines for the four alkyl halides against the corresponding halogen atom ionization potential we obtain a linear correlation, Figure 2. It is instructive also to compare the slopes in entries 13–15. The trend is that the "methylene volume" decreases from the free acid through the methyl ester to the ethyl ester, i.e., with increasing size of R′ in COOR′ (R′ = H, Me, Et). If we compare the methylene contribution to the molar volume of *n*-alkanols, entry 8, and that of the corresponding acetates, entry 14, Table I, we see a considerable increase

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[13] Partington, J. R. *An Advanced Treatise on Physical Chemistry*; Vol. 2, p 17.

[14] Meyer, A. Y. *Chem. Soc. Rev.* **1986**, *15*, 449.

[15] Molecular weights and densities are from *Handbook of Chemistry and Physics*, 54th ed.; CRC Press: Boca Raton, FL, 1973–74.

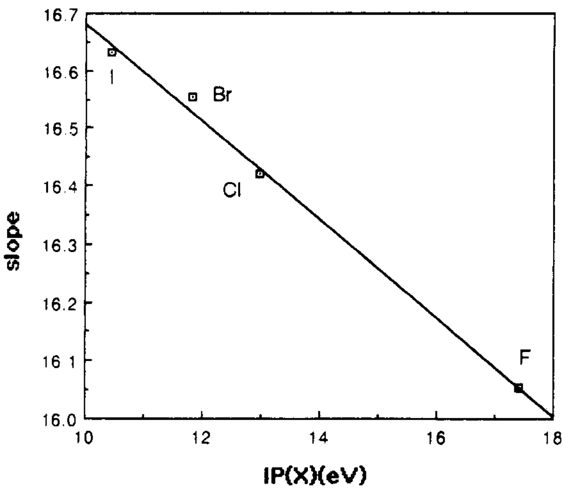

Figure 2. Slopes of the regression V_M vs n lines for n-alkyl halides plotted against the ionization potential of the halogen atom in n-RX.

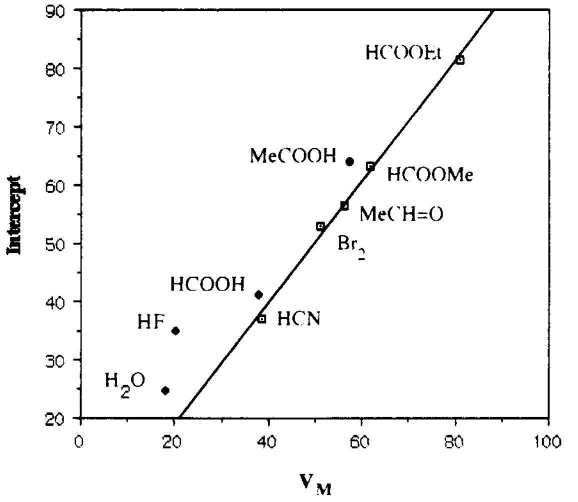

Figure 3. Intercepts of the regression V_M vs n lines of Table I plotted against the corresponding molar volumes of the "parent" compounds (see text).

of the space requirement by a methylene group in n-alkanols upon esterification, i.e., 16.629 versus 16.745 cm^3.

Now let us examine the intercepts of the regression lines in Table I. Our statement that the intercept should correspond to the contribution of the parent compound to the value of the MV, appears to be justified only in some cases. These are entries 7, 12, 13, 16, and 18, which correspond to the parent compounds, HCN, HCOOMe, HCOOEt, $CH_3CH{=}O$, and Br_2, whereas disagreement between intercept and MV's of the parent compounds is observed for HF, H_2O, HCOOH, and CH_3COOH, entries 3, 8, 11, and 14, respectively. The latter set of compounds involves more or less strong hydrogen bonding, and this might be an obvious reason for the observed disagreement. In these cases the actual MV is considerably smaller than the one predicted from the intercept, and this can be readily attributed to the association of the H-bonded molecules. This can be seen by examining Figure 3, in which intercepts are plotted against the corresponding molar volumes of the parent compounds. Those points which correspond to compounds without H-bonds are on the regression line, whereas the points that correspond to H-bonded molecules deviate markedly.

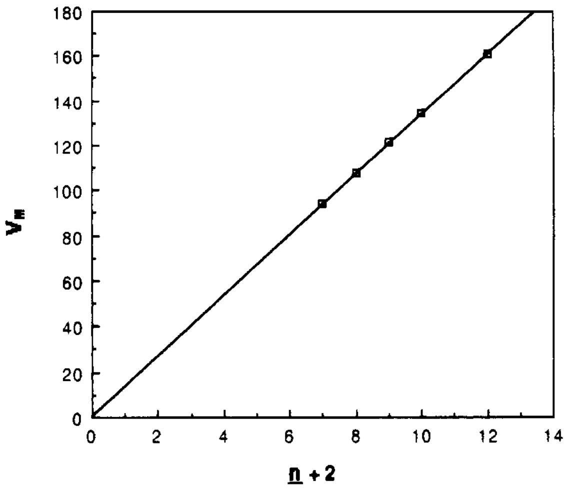

Figure 4. Molar volumes of cycloalkanes plotted against (n + 2), where n is the corresponding carbon number. (Notice that the straight line passes through the origin.)

The above analysis of the intercepts certainly breaks down in the case of entry 2, Table I, referred to cycloalkanes. The MV vs n regression line for cycloalkanes $(CH_2)_n$ should pass through the origin, but instead it exhibits an intercept of 27.61 cm^3. The slope of the regression line for cycloalkanes has a markedly lower value than that for normal alkanes, namely 13.35 versus 16.32 cm^3 per methylene group, entries 1–2, Table I. Thus, the demand for space by a methylene group in a cycloalkane appears to be less than the space required by a methylene group in n-alkanes. This, perhaps, could be understood on the basis that in a liquid the space requirement by a molecule is larger than the actual size of the molecule or, in other words, in a liquid there is some empty space between molecules.[14] The empty space in cycloalkanes is relatively small, due to their denser packing.[14] It is more difficult to explain the finite intercept in the case of cycloalkanes. One could be tempted to associate the intercept of 27.61 cm^3 to the free space. However, in such a case any of the slopes in Table I should be considerably larger than the MV of the parent compound, which is not the case. It could be of interest to note that a plot of the MV of cycloalkanes against $n + 2$ gives a straight line passing very nearly through the origin, Figure 4. In other words, the intercept is approximately twice the slope of the regression line, entry 2, Table I. Thus, cycloalkanes appear to be derived from the imaginary "parent compound" CH_2CH_2.

As a corollary of the MV vs n linear relationship which holds for the n-alkyl derivative members of any homologous series, it follows that the MV's of the n-alkyl derivatives should be interrelated. Indeed, Figure 5 indicates that this is the case. However in Figure 5 the branched alkyl derivatives are included as well, and these too seem to obey the linearity expected for the n-alkyl derivatives only. If one plots the MV's of, e.g., n-pentyl halides, n-$C_5H_{11}X$ (X = F, Cl, Br, and I) against the corresponding MV's of any RX, e.g., n-decyl halides, one obtains a straight line Figure 6. The latter correlation, in conjunction with that of Figure 5, implies that MV's of alkyl halides cross-correlate.

Molar Volumes and Normal Boiling Points. Molar volume is involved in the Lorentz–Lorentz equation (1) which connects molecular refractivity and polarizability.

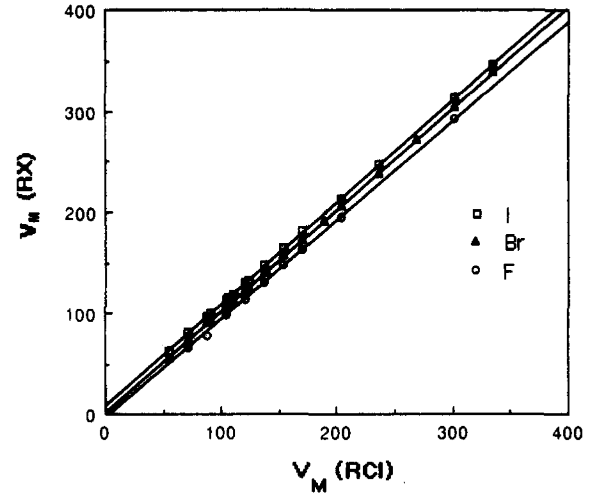

Figure 5. Molar volumes of alkyl fluorides, bromides, and iodides plotted against the corresponding MV's of alkyl chlorides. (Note that all isomers are included in the correlations.)

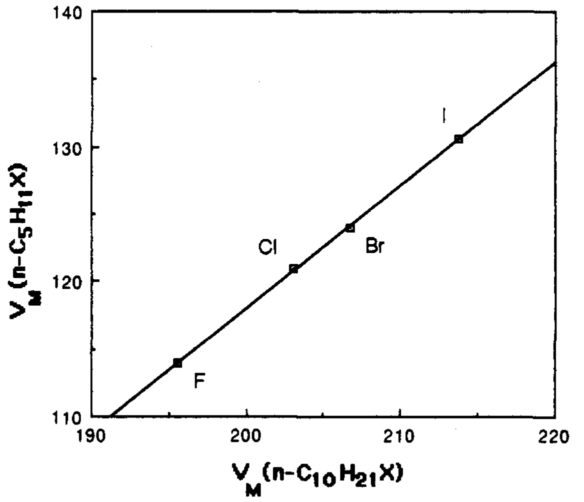

Figure 6. Molar volumes of *n*-pentyl halides plotted against the MV's of the corresponding *n*-decyl halides.

Recently, we have shown[16] that the latter parameters correlate with normal boiling points. This then prompted us to search for relationships between MV's and normal boiling points. The molar volumes of di- and trihalomethanes seem to plot linearly against the respective normal boiling points, Figure 7. The MV's of homologous series of, e.g., *n*-alkyl halides do not plot linearly against the respective normal bp's, but the ratio V_M/T_b, where T_b is the normal bp in K, does, with the exception of the first few points, e.g., Figure 8. Table II summarizes the regression V_M/T_b vs n equations for various homologous series. It should be noted that, with the exception of normal alkanes, the deviations of the first few points from the regression line are negative. Interestingly enough, for the sequences of the symmetric compounds, entries 17 and 18, there are no deviating points from the regression line. The same is true for cycloalkanes for which, however, data for $n = 3$ and 4 are missing.

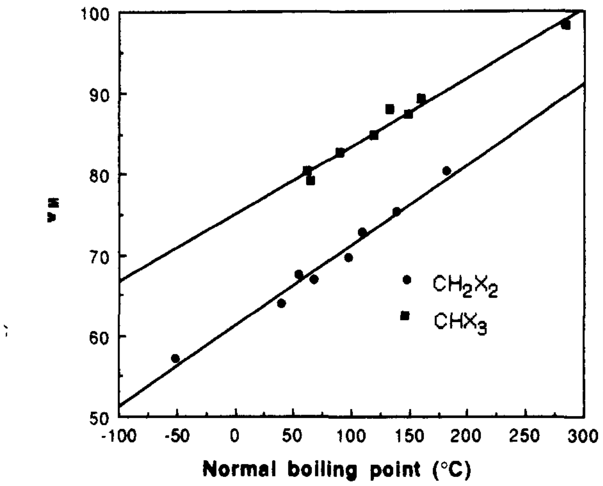

Figure 7. Molar volumes of di- and trihalomethanes plotted against the corresponding normal boiling points.

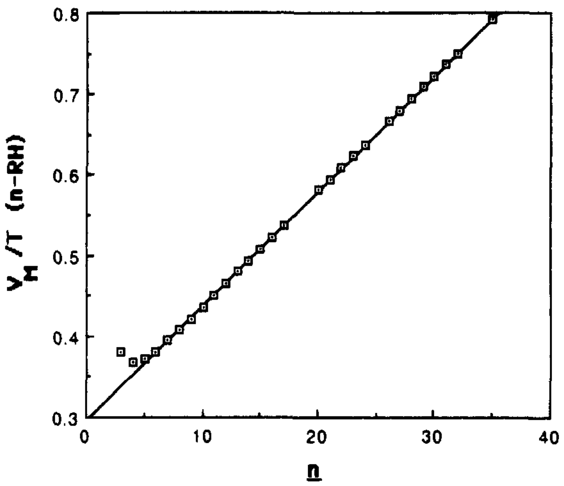

Figure 8. Ratios of (molar volume at 20 °C)/(normal boiling point in absolute temperature) plotted against the corresponding carbon numbers.

Table II. Regression Equations of V_M/T_b vs n Plots and Relevant Data

entry no.	*n*-RX	slope	intercept	*r*	range of *n*[a]
1	*n*-RH	0.014 23	0.295 40	1.000	5–35
2	cycloalkanes	0.009 11	0.247 22	0.990	5–10
3	*n*-RF	0.016 79	0.255 98	0.999	4–16
4	*n*-RCl	0.017 14	0.234 19	0.999	4–18
5	*n*-RBr	0.017 68	0.221 72	0.999	4–17
6	*n*-RI	0.017 38	0.218 90	0.999	4–18
7	*n*-RCN	0.018 68	0.189 66	0.999	6–17
8	*n*-ROH	0.023 69	0.145 09	0.997	4–10
9	*n*-RSH	0.019 32	0.211 76	0.998	3–10
10	*n*-RNH_2	0.017 77	0.219 54	0.998	6–16
11	*n*-RCOOH	0.024 07	0.140 17	0.999	3–8
12	*n*-RCOOMe	0.019 89	0.246 26	0.998	3–11
13	*n*-RCOOEt	0.018 89	0.278 75	0.999	3–11
14	MeCOOR-*n*	0.019 84	0.249 89	0.999	3–10
15	*n*-R^1SR^2-*n*	0.018 80	0.222 04	0.996	4–10
16	*n*-RCOMe	0.020 79	0.224 45	0.998	3–10
17	$Cl(CH_2)_nCl$	0.019 80	0.183 81	0.999	1–6
18	$Br(CH_2)_nBr$	0.021 29	0.168 53	0.997	1–5
19	*n*-$RCH{=}CH_2$	0.014 69	0.309 54	1.000	4–14

[a] The upper limit of the indicated range is determined by the availability of data, whereas the lower one denotes the first member of the series which complies with the linear relationship.

The V_M/T_b parameters behave like the corresponding thermochemical parameters, i.e., $\Delta H_v/T_b$ or $\Delta H_f/T_b$ parameters.[3,16] Namely, the parameters V_M/T_b for any two series of monofunctional derivatives of aliphatic hydrocarbons plot linearly against each other, e.g., Figure 9. Of course, the linearity of Figure 9 could be viewed as a corollary of the V_M/T_b vs n correlations, but it should be

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(16) Screttas, C. G.; Micha-Screttas, M., submitted.

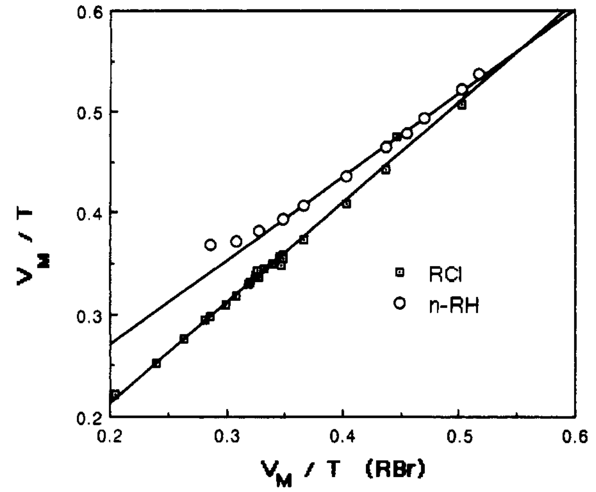

Figure 9. Ratios of V_M/T_b of alkyl chlorides and of normal hydrocarbons plotted against the corresponding V_M/T_b rations of alkyl bromides.

born in mind that the latter correlations hold for the *n*-alkyl derivatives only, whereas in Figure 9 are included the branched alkyl derivatives as well. The linearity between V_M/T_b and n and between V_M and n permits the estimation of normal boiling points of *n*-alkyl derivatives. For example, we can estimate the MV of 1-pentadecylamine from the regression equation entry 10, Table I: $V_M = (16.577)(15) + 32.266 = 280.921$ cm^3, and from regression equation entry 10, Table II, we can obtain $V_M/T_b = (0.01777)(15) + 0.221\,954 = 0.486\,09$. The ratio of the two numbers should give T_b. Namely, 280.921/0.48609 = 577.9 K, or 304.8 °C. This result agrees fairly well with the experimental t_b (760 mm/Hg) = 307.6 °C.

Transferability and Additivity of Molar Volumes. A phenomenon analogous to reaction thermoneutrality seems to hold for MV's also. Indeed, if we consider reaction 3 and compare the sum of the MV's of the "reactants" with the sum of the MV's of the "products" we see that the two sums are very nearly equal. This implies that the alkyl and functional group contributions to the molar volumes are transferable and additive. Further examples are given in eqs 4–12.

$$2\ \mathrm{Et(Me)CHBr} \rightarrow \mathrm{Me_2CHBr} + \mathrm{Et_2CHBr} \qquad (3)$$

$$2(108.884) = 217.768 \rightarrow 93.607 + 124.588 = 218.195\ (\Delta V_M = 0.427\ \mathrm{cm^3})$$

$$n\text{-BuI} + \mathrm{EtBr} \rightarrow n\text{-BuBr} + \mathrm{EtI} \qquad (4)$$

$$113.916 + 74.617 = 188.533 \rightarrow 107.407 + 80.571 = 187.571\ (\Delta V_M = -0.962\ \mathrm{cm^3})$$

$$s\text{-BuBr} + n\text{-C}_5\mathrm{H}_{11}\mathrm{I} \rightarrow s\text{-BuI} + n\text{-C}_5\mathrm{H}_{11}\mathrm{Br}$$

$$108.884 + 130.631 = 239.515 \rightarrow 115.590 + 123.994 = 239.584\ (\Delta V_M = 0.069\ \mathrm{cm^3})$$

$$\mathrm{CH_3COOMe} + \mathrm{CH_3CH_2COOEt} \rightarrow \mathrm{CH_3COOEt} + \mathrm{CH_3CH_2COOMe} \qquad (5)$$

$$79.400 + 114.534 = 193.934 \rightarrow 97.878 + 96.306 = 194.184\ (\Delta V_M = 0.25\ \mathrm{cm^3})$$

$$s\text{-PrI} + n\text{-C}_5\mathrm{H}_{11}\mathrm{Br} \rightarrow s\text{-PrBr} + n\text{-C}_5\mathrm{H}_{11}\mathrm{I} \qquad (6)$$

$$99.800 + 123.994 = 223.794 \rightarrow 93.607 + 130.631 = 224.238\ (\Delta V_M = 0.444\ \mathrm{cm^3})$$

$$\mathrm{EtBr} + n\text{-BuCl} \rightarrow \mathrm{EtCl} + n\text{-BuBr} \qquad (7)$$

$$74.617 + 104.457 = 179.074 \rightarrow 107.407 + 71.865 = 179.272\ (\Delta V_M = 0.198\ \mathrm{cm^3})$$

$$n\text{-BuCN} + n\text{-C}_7\mathrm{H}_{15}\mathrm{Br} \rightarrow n\text{-BuBr} + n\text{-C}_7\mathrm{H}_{15}\mathrm{CN} \qquad (8)$$

$$103.809 + 157.114 = 260.923 \rightarrow 153.909 + 107.407 = 261.316\ (\Delta V_M = 0.393\ \mathrm{cm^3})$$

$$2n\text{-BuSMe} \rightarrow n\text{-Bu}_2\mathrm{S} + \mathrm{Me_2S} \qquad (9)$$

$$2(123.689) = 247.378 \rightarrow 174.457 + 73.241 = 247.698\ (\Delta V_M = 0.320\ \mathrm{cm^3})$$

$$2\mathrm{CH_2BrCl} \rightarrow \mathrm{CH_2Br_2} + \mathrm{CH_2Cl_2} \qquad (10)$$

$$2(66.889) = 133.778 \rightarrow 69.624 + 64.021 = 133.645\ (\Delta V_M = -0.133\ \mathrm{cm^3})$$

$$n\text{-PrI} + 1\text{-ClC}_{10}\mathrm{H}_7 \rightarrow n\text{-PrCl} + 1\text{-IC}_{10}\mathrm{H}_7 \qquad (11)$$

$$97.198 + 136.221 = 233.419 \rightarrow 88.158 + 146.026 = 234.184\ (\Delta V_M = 0.765\ \mathrm{cm^3})$$

$$\mathrm{PhI} + 1\text{-ClC}_{10}\mathrm{H}_7 \rightarrow \mathrm{PhCl} + 1\text{-IC}_{10}\mathrm{H}_7 \qquad (12)$$

$$111.432 + 136.221 = 247.653 \rightarrow 101.791 + 146.026 = 247.817\ (\Delta V_M = 0.164\ \mathrm{cm^3})$$

Reactions 3–12 are either disproportionation or redistribution reactions, and in all cases the hydrocarbyl group is transferred intact and the number of molecules remains constant. Now, if we consider a reaction in which molecular fragments are redistributed, e.g., eqs 13 and 14, we see that again the sum of the molar volumes of the "reactants" is nearly equal to the sum of MV's of the "products".

$$n\text{-C}_8\mathrm{H}_{18} + n\text{-BuBr} \rightarrow n\text{-C}_{10}\mathrm{H}_{22} + \mathrm{EtBr} \qquad (13)$$

$$162.605 + 107.407 = 270.012 \rightarrow 194.918 + 74.617 = 269.535\ (\Delta V_M = -0.477\ \mathrm{cm^3})$$

By "transferring" various molecular fragments from *n*-BuBr to *n*-octane or vice versa, it can be shown that the smallest ΔV_M value occurs for the smallest possible changes, namely on going to *n*-heptane + *n*-pentyl bromide ($\Delta V_M = 0.539$) or to *n*-nonane + *n*-propyl bromide ($\Delta V_M = -0.415$). In general, the ΔV_M values became increasingly negative on elongating the *n*-alkane and increasingly positive on shortening it.

$$n\text{-C}_8\mathrm{H}_{18} + \mathrm{Br_2} \rightarrow n\text{-C}_7\mathrm{H}_{15}\mathrm{Br} + \mathrm{CH_3Br} \qquad (14)$$

$$162.605 + 51.237 + 213.842 \rightarrow 157.114 + 56.664 = 213.774\ (\Delta V_M = -0.068\ \mathrm{cm^3})$$

We notice that alternative "partitioning" of *n*-octane and a bromine molecule to give the pairs of alkyl bromides, $n\text{-C}_6\mathrm{H}_{13}\mathrm{Br}$ – EtBr, $n\text{-C}_5\mathrm{H}_{11}\mathrm{Br}$ – *n*-PrBr, and *n*-BuBr – *n*-BuBr, leads to the ΔV_M values 1.34, 1.014, and 0.972 cm^3, respectively. However, the equality of the molar volumes does not hold in the addition reaction 15.

$$n\text{-BuCH}{=}\mathrm{CH_2} + \mathrm{Br_2} \rightarrow n\text{-BuCH(Br)CH}_2\mathrm{Br} \qquad (15)$$

$$125.033 + 51.237 = 176.270 \rightarrow 154.672\ (\Delta V_M = -21.598\ \mathrm{cm^3})$$

Another case where equality of MV's does not hold is for reactions involving "reactants" or "products" with strong hydrogen bonding, e.g., eq 16

$$n\text{-}C_8H_{18} + H_2O \rightarrow n\text{-}C_7H_{16} + CH_3OH \qquad (16)$$

$$162.605 + 18.02 = 180.625 \rightarrow 146.570 + 40.485 = 187.055\ (\Delta V_M = 6.43\ \text{cm}^3)$$

It can be seen that in most cases the two sums differ by less than 0.5 cm^3. It is interesting to note that for the examples in eqs 11 and 12 the latter gives a better agreement, namely, to within 0.765 versus 0.164 cm^3, respectively. Equation 12 involves aromatic compounds only, and their close structural analogy could be the reason for the observed better agreement. The above phenomenon, by analogy to thermoneutrality, may be termed "choroneutrality" (χῶρος = space). It seems, from the example in eq 15, that a basic condition for "choroneutrality" to hold is that the number of molecules remains constant. It seems also that reactions involving reactants and products with strong hydrogen bonds are not "choroneutral".

Under the assumption that "choroneutrality" holds, one could use a reaction like (3–12) for obtaining an estimate of the density for a compound. For example, if we wish to obtain an estimate of the density of 1-iodonaphthalene, we can first obtain an estimate of its MV from eq 12, and from this and the corresponding molecular weight we can calculate the density, eq 17

$$V_M(1\text{-}IC_{10}H_7) = V_M(PhI) + V_M(1\text{-}ClC_{10}H_7) - V_M(PhCl) = 111.432 + 136.221 - 101.791 = 145.862\ \text{cm}^3 \qquad (17)$$

$\rho(1\text{-}IC_{10}H_7) = 254.07/145.863 = 1.7418\ \text{g/cm}^3$ (experimental 1.7399 g/cm^3) at 20 °C. The two numbers agree to the 2nd decimal point.

Molar Volumes and Solubility. According to Hildebrand's theory for "regular solutions"[8] solubility is correlated with the square root of the expression (2) which is termed solubility function, δ. When the solvent is varied within a homologous series, such as normal hydrocarbons, and one plots solubility of a given solute to the hydrocarbon solvents against δ, one obtains a concave correlation. We found that a better correlation is obtained by plotting solubility against molar volume of the solvent. This is exemplified by the plot in Figure 10, where molar volumes of C_5–C_{14} n-alkanes seem to plot fairly linearly against the corresponding solubilities of the C_{60} fullerene.[10,17]

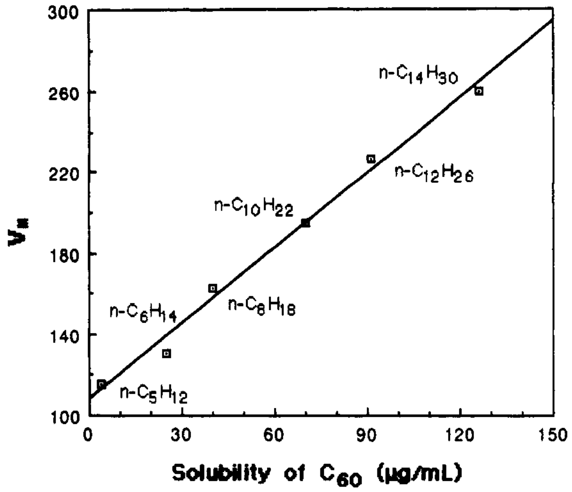

Figure 10. Molar volumes of normal alkanes plotted against the solubility of C_{60} in the same solvents.

Conclusions

It has been shown that the molar volumes of 20 °C of any two series of monofunctional derivatives of aliphatic hydrocarbons plot linearly against each other. The methylene group contribution to the molar volume of an n-alkyl derivative is transferable and additive in an intraseries fashion, and its space requirement exhibits a small but significant dependence even on secondary changes on the functional group, e.g., n-RCOOMe vs n-RCOOEt. It has been shown that the parameter V_M/T_b behaves like a thermochemical one. A phenomenon analogous to reaction thermoneutrality seems to hold for molar volumes as well, namely, "choroneutrality". From choroneutral reaction one can obtain estimates of molar volumes and/or densities.

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(17) For correlations between calculated volume or surface area and solubility see: Funasaki, N.; Hada, S.; Neya, S.; Machida, K. *J. Colloid Interface Sci.* **1985**, *106*, 255. Pearlman, R. S.; Yalkowski, S. H.; Banerjee, S. *J. Phys. Chem. Ref. Data* **1984**, *13*, 555. Iwase, K.; Komatsu, K.; Hirono, S.; Nakagawa, S.; Moriguchi, I. *Chem. Pharm. Bull.* **1985**, *33*, 2114.